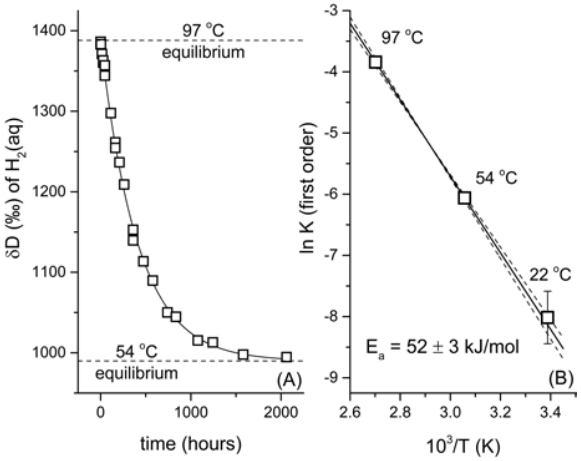
Kinetics of D/H fractionation between H_2O and dissolved H_2 at hydrothermal conditions

N. PESTER[1, 2], M. CONRAD[1], K. KNAUSS[1]

[1]Lawrence Berkeley National Laboratory, Berkeley CA, USA
[2]corresponding email: njpester@lbl.gov

Dissolved H_2 is common in crustal fluids attending mineral hydration over a range of physical conditions. The D/H fractionation factor between H_2O and H_2 varies as a function of temperature with implications for geothermometry when sampling natural springs. Equilibrium fractionation is reasonably constrained, but there are no data on equilibration rates in condensed H_2O that would allow interpretation of residence times for subsurface fluid flow. We have perfomed kinetic experiments in a flexible gold cell between 20 and 100 °C at 70 bars. This cell minimizes surface catalysis and allowed us to maintain pressure during time series sampling, ensuring H_2 remained undersaturated (i.e. no gas headspace or bubbles). The latter is important because the presence of a gas phase creates ambiguity in that $H_2(g) \leftrightarrow H_2(aq)$ exchange appears to be rate limiting. A heavy starting water was used (~5250‰) such that variability of δD_{H2O} was negligible, and isothermal changes in the δD of H_2 (18 mmolal) were used to derive first order rate constants, exemplified below (A). At 22



°C, equilibration took over 1.3 yrs whereas extrapolation of the Arrhenius relationship (B) suggests equilibrium is essentially instantaneous for T > ~200°C. These data are readily applicable to systems reflecting serpentinization at moderate T, an example being the Lost City hydrothermal field, where D/H fractionation in the fluid reflects higher T than measured during sample aquisition at the seafloor[3].

[3] *Proskurowski et al. (2006) Chem. Geol. 229, p331-343*